Activation of Terminal Alkynes with *cis*-[$RuCl_2(Ph_2PCH_2PPh_2)_2$]: New Vinylidene– and Acetylide–Ruthenium Complexes and Crystal structures of [$(Ph_2PCH_2PPh_2)_2(Cl)Ru{=}C{=}CH_2$]$PF_6$ and [$(Ph_2PCH_2PPh_2)_2(Cl)RuC{\equiv}CH$] Complexes

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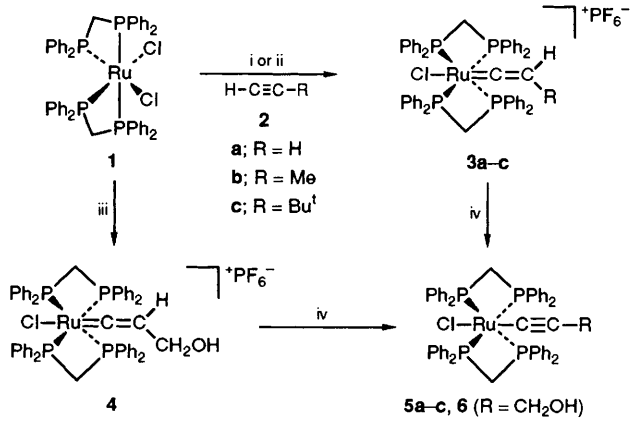
The activation of alkynes HC≡CR with *cis*-[$RuCl_2(Ph_2PCH_2PPh_2)_2$] **1** leads to vinylidenes *trans*-[$(Ph_2PCH_2PPh_2)_2(Cl)Ru^+{=}C{=}CHR$], even directly from acetylene itself (R = H) or prop-2-ynyl alcohol, from which the $Ru^+{=}C{=}CH(CH_2OH)$ moiety is resistant to dehydration, and deprotonation with 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) directly affords *trans*-[$(Ph_2PCH_2PPh_2)_2(Cl)Ru{-}C{\equiv}C{-}R$] derivatives.

Vinylidene metal complexes have recently found increasing interest resulting from the activation of terminal alkynes with 16-electron metal species and as a preliminary step for the synthesis of metal carbene derivatives.[1] Ruthenium(II) complexes, especially $[Ru(PR_3)_2(C_5H_5)]^+$ moieties, have played an important role for the study of tautomerism of [$Ru(\eta^2$-HC≡CR)] complexes and the stabilisation of [$Ru(\eta^1$-C=CHR)] derivatives,[1,2] whereas the electrophilic $[RuCl_2(PR_3)(arene)]$ derivatives give very reactive vinylidene intermediate precursors of carbene.[3] We now report (*i*) that *cis*-

$[RuCl_2(Ph_2PCH_2PPh_2)_2]$ **1** readily activates terminal alkynes to produce new vinylidene ruthenium complexes **3** but its behaviour contrasts with both $Ru(C_5H_5)$ and $Ru(C_6R_6)$ precursors as it allows the straightforward access, directly from acetylene, to the stable $[(dppm)_2(Cl)Ru{=}C{=}CH_2]^+$ cation **3a** (92%) [dppm = bis(diphenylphosphino)methane] and gives evidence for the formation of the $[Ru{=}C{=}CH\text{-}CH_2OH]^+$ moiety as the first step in the activation of prop-2-ynyl alcohol, (*ii*) the most efficient route to acetylide–ruthenium(II) complexes from alkynes *via* deprotonation of vinylidenes and (*iii*) the X-ray structural determination of related complexes containing the $Ru^+{=}C{=}CH_2$ and Ru–C≡CH moieties.

The reaction of **1** with an excess of acetylene dissolved in dichloromethane, without a halide abstracting reagent but with $NaPF_6$ at room temperature, leads to the formation of the orange *trans*-chloro vinylidene salt **3a** (92%).† Analogously, propyne and *tert*-butylacetylene are activated by complex **1** to give the orange vinylidene complexes **3b** (97%) and **3c** (84%),† respectively (Scheme 1). These compounds show in the IR an absorption at ~1650 cm^{-1} [$\nu_{C=C}$] and in ^{13}C NMR a low field quintuplet for the C=Ru carbon nucleus due to the coupling with four equivalent *cis* ^{31}P nuclei (**3a**: δ 340.8, $^2J_{P,C}$ 13.1 Hz) and a high field *C*=C=Ru signal [**3a**: δ 91.4 (t, quint.), $^3J_{P,C}$ 1.9 Hz, $^1J_{C,H}$ 165.6 Hz].

It is noteworthy that **3a** is rapidly formed directly from acetylene itself, whereas the $[(C_5H_5)(R_3P)_2Ru^+{=}C{=}CH_2]$ intermediates were conveniently obtained from HC≡C-$SiMe_3$ and methanol,[2a,b] or *via* protonation of corresponding acetylide.[2c] **3a** is also very stable toward addition of methanol in contrast to the $Ru(C_5H_5)$[2] or $Ru(C_6R_6)$[3] derivatives, probably because of the protection of the Ru=C= carbon by both the electron-rich $[Ru(dppm)_2Cl]$ moiety and the steric hindrance of four phenyl groups (Fig. 1). The exceptional stability of **3a**



Scheme 1 *Reagents and conditions*: i, **1** (0.5 mmol), $NaPF_6$ (2 equiv.) CH_2Cl_2 (50 ml) saturated with acetylene **2a** at P = 1 atm, room temp. for 4 h; ii, **2b–2c** (2 equiv.), CH_2Cl_2 (50 ml), $NaPF_6$ (2 equiv.), room temp., 4 h; iii, **1** (0.5 mmol), $HC{\equiv}CCH_2OH$ (1.1 mmol), $NaPF_6$ (1 mmol) in CH_2Cl_2 (60 ml) at room temp. for 4 h; iv, DBU (1 equiv.) in dichloromethane, room temp., 1 h

allowed its single crystal X-ray structural analysis.‡ The first structural characterization of a complex containing the $M{=}C{=}CH_2$ moiety has only just been reported for $[Ru{=}C{=}CH_2(PMe_2Ph)_2(C_5H_5)]BF_4$.[2c] The ORTEP plot for **3a** (Fig. 1) shows the presence of the linear vinylidene group in a *trans* position to the chlorine atom. The most important fact is the very short bond distance C(3)–C(4) [1.22(1) Å] as compared with the C≡C distance (1.20–1.21 Å) and with other ruthenium–vinylidene analogous C=C bond lengths, 1.313(10) Å for $[Ru(PMe_3)_2(C_5H_5)(C{=}CHMe)]PF_6$,[4] 1.25(1) Å for [Ru(prophos)$(C_5H_5)(C{=}CHMe)]PF_6$[5] and 1.287(13) Å for $[Ru{=}C{=}CH_2(PMe_2Ph)_2(C_5H_5)]BF_4$;[2c] [prophos = (*R*)-1,2-bis-(diphenylphosphino)propane]. This observation is consistent with a partial sp character of the C-4 carbon, according to its ^{13}C NMR shift (δ 91.7).

The activation of prop-2-ynyl alcohol derivatives is of special interest as it was observed to lead to the dehydration of the $HC{\equiv}CCR_2OH$ unit on coordination to ruthenium(II)[1c,6] and then give addition of 1 or 2 moles of alcohol to produce carbenes.[7] Complex **1** reacts with $HC{\equiv}CCH_2OH$ to give the stable light-brown complex **4** (76%)† which surprisingly appears to be resistant to dehydration. This evidence for the HC≡C hydrogen 1,2-shift, which was previously observed only with the $Mn(CO)_2(C_5H_5)$ derivative,[1b] strongly supports that such a shift is the initial step leading to dehydration into allenylidene ruthenium intermediates.[6,7]

The short $(RuC_2H_2)C{=}C$ bond length of **3a** and the chemical shifts of =CHR groups suggested that complexes **3** were strongly acidic. Actually, complexes **3a–c** can be deprotonated either with $NaBH_4$ in tetrahydrofuran or by treatment with

† Satisfactory elemental analyses were obtained for all derivatives.

Selected spectroscopic data for **3a**: IR ν/cm^{-1} (KBr) 1627s (C=C); $^{31}P\{^1H\}$ NMR (121.50 MHz, CD_2Cl_2) δ −15.17 (s, Ph_2P), −143.9 (sept, PF_6^-); ^1H NMR (300.134 MHz, CD_2Cl_2) δ 2.36 (quint, $=CH_2$, $^4J_{P,H}$ 3 Hz).

3b: IR ν/cm^{-1} (KBr) 1658s (C=C); $^{31}P\{^1H\}$ NMR (121.50 MHz, CD_2Cl_2) δ −15.08 (s, Ph_2P); ^1H NMR (300.13 MHz, CD_2Cl_2) δ 2.57 (q, quint, =CH, $J_{H,H}$ 7.6, $J_{P,H}$ 2.8 Hz), 0.49 (d quint, =CMe, $J_{P,H}$ 0.8 Hz); $^{13}C\{^1H\}$ NMR (75.47 MHz, CD_2Cl_2) δ 321.1 (quint, Ru=*C*, $^2J_{P,C}$ 13 Hz), 100.5 (br s, Ru=C=*C*).

3c: IR ν/cm^{-1} (KBr) 1644s (C=C); ^{31}P $\{^1H\}$ NMR (121.50 MHz, CD_2Cl_2) δ −15.01 (s, Ph_2P); ^1H NMR (300.13 MHz, CD_2Cl_2) δ 1.79 (quint, =CH, $J_{P,H}$ 2.2 Hz); 0.11 (s, Bu^t); $^{13}C\{^1H\}$ NMR (75.47 MHz, CD_2Cl_2) δ 324.6 (quint, Ru=C, $^2J_{P,C}$ 13 Hz), 117.6 (quint, Ru=C=C, $^3J_{P,C}$ 3.3 Hz).

4: IR ν/cm^{-1} (KBr) 1658s (C=C); $^{31}P\{^1H\}$ NMR (121.50 MHz, CD_2Cl_2) δ −15.24 (s, Ph_2P), −143.4 (sept, PF_6^-); ^1H NMR (300.13 MHz, CD_2Cl_2) δ 3.02 (m, =CH), 2.81 (d, CH_2OH, $^3J_{H,H}$ 8.2 Hz) 0.4 (br s, OH); $^{13}C\{^1H\}$ NMR (75.47 MHz, CD_2Cl_2) δ 351.4 (quint, Ru=C, $^2J_{P,C}$ 13.5 Hz), 107.3 (quint, Ru=C=*C*, $^3J_{P,C}$ 2.1 Hz).

5a: IR ν/cm^{-1} (KBr) 3289 (≡CH), 1935s (C≡C); $^{31}P\{^1H\}$ NMR (121.50 MHz, CD_2Cl_2) δ −5.4 (s, Ph_2P); ^1H NMR (300.13 MHz, CD_2Cl_2) δ 0.88 (quint, ≡CH, $^4J_{P,H}$ 1.7 Hz); ^{13}C $\{^1H\}$ NMR (75.47 MHz, CD_2Cl_2) δ 112.0 (quint, Ru–C, $^2J_{P,C}$ 15.2 Hz), 97.4 (quint, Ru–C≡*C*, $^3J_{P,C}$ 2 Hz).

5b: IR ν/cm^{-1} (KBr) 2107s (C≡C); $^{31}P\{^1H\}$ NMR (121.50 MHz, CD_2Cl_2) δ −5.63 (s, Ph_2P); ^1H NMR (300.13 MHz, CD_2Cl_2) δ 1.04 (quint, Me, $^5J_{P,H}$ 1.7 Hz); ^{13}C $\{^1H\}$ NMR (75.47 MHz, CD_2Cl_2) δ 96.7 (quint, Ru–C, $^2J_{P,C}$ 15.8 Hz), 103.5 (quint, Ru–C≡*C*, $^3J_{P,C}$ 1.2 Hz).

5c: IR ν/cm^{-1} (KBr) 2087s (C≡C); $^{31}P\{^1H\}$ NMR (121.50 MHz, CD_2Cl_2) δ −5.53 (s, Ph_2P); ^1H NMR (300.13 MHz, CD_2Cl_2) δ 0.31 (s, Bu^t); $^{13}C\{^1H\}$ NMR (75.47 MHz, CD_2Cl_2) δ 91.9 (quint, Ru–C, $^2J_{P,C}$ 15.7 Hz), 118.4 (quint, Ru–C≡*C*, $^3J_{P,C}$ 1.8 Hz).

6: IR ν/cm^{-1} (KBr) 2094s (C≡C); $^{31}P\{^1H\}$ NMR (121.50 MHz, CD_2Cl_2) δ −5.75 (s, Ph_2P); ^1H NMR (300.13 MHz, CD_2Cl_2) δ 3.42 (m, CH_2), −0.44 (t, OH, $J_{H,H}$ 5.2 Hz; $^{13}C\{^1H\}$ NMR (75.47 MHz, CD_2Cl_2) δ 113.4 (quint, Ru–C, $^2J_{P,C}$ 15.2 Hz), 108.6 (s, Ru–C≡*C*).

‡ *Crystal data*: $C_{52}H_{46}ClP_4Ru$, PF_6 **3a**: M_r = 1076.318, orthorhombic, $Pna2_1$, a = 22.603(3), b = 11.850(2), c = 19.235(6) Å, V = 5152(2) Å^3, Z = 4, D_x = 1.39 Mg m^{-3}, λ(Mo-Kα) = 0.71069 Å, μ = 6.15 cm^{-1}, $F(000)$ = 2192, T = 293 K, final R = 0.037 for 3129 observations. The sample (prism 0.15 × 0.23 × 0.32 mm) was studied on an automatic diffractometer CAD4 Enraf-Nonius with graphite monochromatized Mo-Kα radiation. The cell parameters were obtained by fitting a set of 25 high-θ reflections. The data collection [$2\theta_{max}$ = 50°, scan ω/2θ = 1, t_{max} = 60 s, range *hkl*: *h* 0.15, *k* 0.24, *l* 0.28, intensity controls without appreciable decay (0.1%)] gives 6214 reflections from which 4293 with $I > \sigma^3(I)$.

After Lorenz and polarization corrections, the structure was solved with a Patterson map which revealed the Ru atom. After isotopic refinement (R = 0.09), the whole structure was refined by full-matrix least-square techniques with the resulting R = 0.039, R_w = 0.037 and S_w = 2.27.

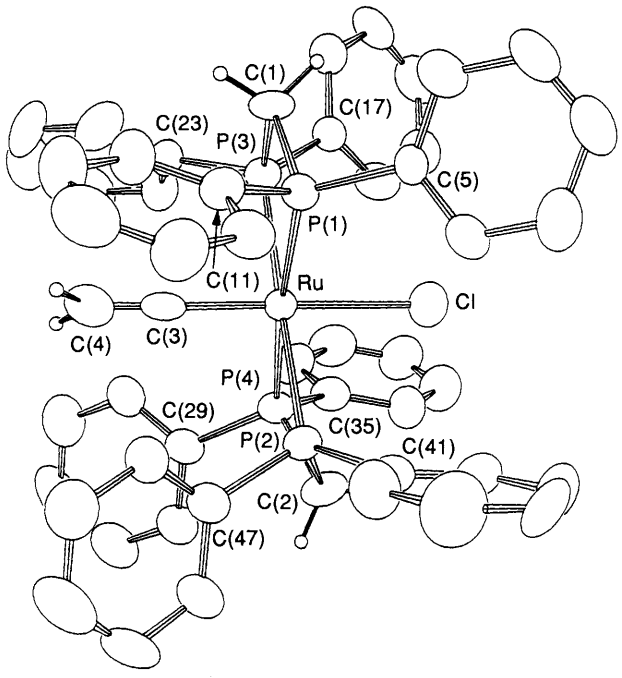


Fig. 1 Molecular structure of cation $[(Ph_2PCH_2PPh_2)_2ClRu{=}C{=}CH_2]^+$ **3a** (ORTEP view). For clarity, hydrogen atoms are omitted. Selected bond distances (Å) and angles (°): Ru–Cl 2.415(2), Ru–P(1) 2.363(2), Ru–P(2) 2.378(2), Ru–P(3) 2.374(2), Ru–P(4) 2.388(2), Ru–C(3) 1.882(8), C(3)–C(4) 1.22(1); Cl–Ru–C(3) 178.8(3), Ru–C(3)–C(4) 178.4(2), P(1)–Ru–C(3) 91.0(3).

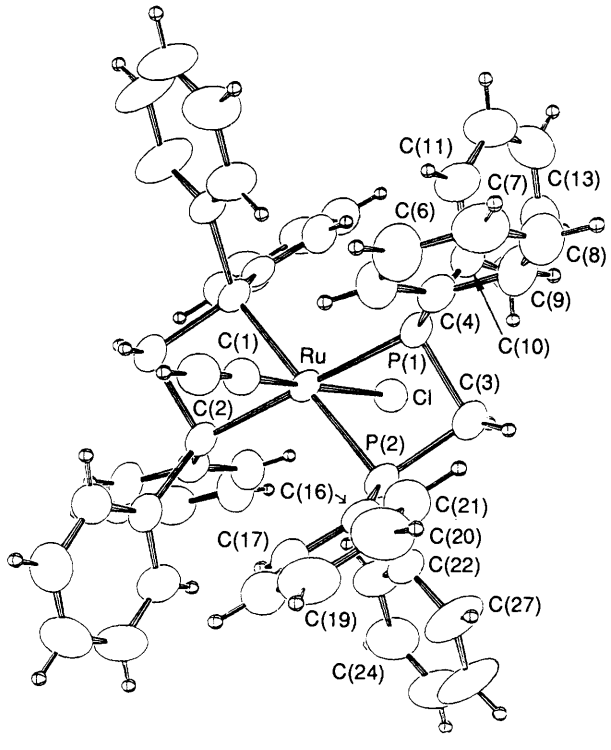


Fig. 2 Molecular structure of $[(Ph_2PCH_2PPh_2)_2ClRu{-}C{\equiv}CH]$ **5a** (ORTEP view). For clarity, hydrogen atoms are omitted. Selected bond distances (Å) and angles (°): Ru–Cl 2.628(2), Ru–P(1) 2.354(1), Ru–P(2) 2.318(1), Ru–C(1) 1.906(9), C(1)–C(2) 1.162(9); Cl–Ru–C(1) 178.2(2), Ru–C(1)–C(2) 177.0(6).

$KOCMe_3$ in CH_2Cl_2, however the best results were obtained by reaction of **3a–c** with DBU (1 equiv.) in dichloromethane which gave the yellow *trans*-chloro acetylide complexes **5a** (47%), **5b** (64%) and **5c** (65%).† These compounds show a C≡C absorption in their IR spectra (1935 cm^{-1} for **5a**) and in ^{13}C NMR two quintuplets for the –C≡C–Ru carbon nuclei (**5a**: C–Ru: δ 112, $^2J_{P,C}$ 15.2 Hz and C≡C–Ru: δ 97.1, $^3J_{P,C}$ 2 Hz). This simple two step **1** → **3** → **5** transformation actually constitutes the best method to selectively produce monoacetylide ruthenium(II) derivatives, for lithium and Grignard reagents, or terminal alkyne and amine, to give low yields of mono- and di-acetylides from **1**. Vinylidene **4** with DBU (1 equiv.) leads to the formation of the hydroxymethylacetylide **6** (45%)† which could not be obtained *via* classical methods.

A single crystal X-ray structural analysis was carried out on complex **5a**§ (Fig. 2). It allows a direct comparison with that of **3a** and shows the *trans* effect of the acetylide ligand on the Ru–Cl bond [2.628(2) Å] which is much longer than that in **3a** [2.451(2) Å]. The most striking observation is related to the C(1)–C(2) bond length [1.162(9) Å] which is very short as compared with 1.199(2) Å observed for $[Ru(CO)_2(C{\equiv}CH)_2(PEt_3)_2]$.[8] It thus appears to be much shorter than the free C≡C bond distance (1.20–1.21 Å).

The easy formation of functional vinylidene ruthenium complexes and their facile deprotonation offer a potential route to unsymmetrically disubstituted acetylide derivatives.

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§ *Crystal data*: $C_{52}H_{45}ClP_4Ru$ **5a**: M_r = 930.36, monoclinic, *I* $2/_a$, *a* = 22.003(2), *b* = 9.715(1) *c* = 22.2025(3) Å, β = 112.38(2)°, *V* = 4389.0(6) $Å^3$, *Z* = 4, D_x = 1.408 Mg m^{-3}, λ(Mo-Kα) = 0.71069 Å, μ = 5.90 cm^{-1}, *F*(000) = 1912, *T* = 293 K, final *R* = 0.024 for 2267 observations. The sample (prism 0.22 × 0.22 × 0.24 mm) was studied on an automatic diffractometer CAD4 Enraf-Nonius with graphite monochromatized Mo-Kα radiation. The cell parameters are obtained by fitting a set of 25 high-θ reflections. The data collection [$2\theta_{max}$ = 50°, scan ω/2θ = 1, t_{max} = 60 s, range *hkl*: *h* 0.25, *k* 0.12, *I* 26.26, intensity controls without appreciable decay (0.4%)] gives 4281 reflections from which 2267 independent (R_{int} = 0.011) with $I > \sigma^3(I)$.

After Lorenz and polarization corrections, the structure was solved with direct methods which revealed all the non-hydrogen atoms of the structure except the two acetylenic carbon atoms. These were found after a scale factor refinement and on Fourier difference. The whole structure was refined by the full-matrix least-square techniques with the resulting *R* = 0.027, R_w = 0.024 and S_w = 1.135.

For both structures the atomic scattering factors were from international tables for X-ray crystallography (1974). All the calculations were performed on a Digital Micro VAX 3100 computer with the MolEN package (Enraf-Nonius, 1990). Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.